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An Assessment of the Long-Term Precision of Continuous Emission Monitors

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The EPA has promulgated regulations requiring certain stationary sources to show continual compliance with emission limits, by using a Continuous Emission Monitoring System (CEMS). In order to make reliable compliance determinations, the quality of the monitoring data is important. Two principal parameters in assessing and describing data quality are precision and accuracy. This paper discusses the long-term precision for five CEMS's installed at scrubber-controlled, coal-fired power plants. Precision estimates were made by utilizing available daily calibration drift data. Six to seven months of calibration drift data were analyzed for each pollutant (SO_2, NO_x) and diluent (O_2, CO_2) analyzer in the CEMS. Results show that most of the monitors exhibited significant bias and variance over the months involved. Monitoring data precision varied significantly from month to month and does not appear to be related to monitor type or manufacturer.

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ABSTRACT

The EPA has promulgated regulations requiring certain stationary sources to show continual compliance with emission limits, by using a Continuous Emission Monitoring System (CEMS). In order to make reliable compliance determinations, the quality of the monitoring data is important. Two principal parameters in assessing and describing data quality are precision and accuracy. This paper discusses the long-term precision for five CEMS's installed at scrubber-controlled, coal-fired power plants. Precision estimates were made by utilizing available daily calibration drift data. Six to seven months of calibration drift data were analyzed for each pollutant (SO_2, NO_x) and diluent (O_2, CO_2) analyzer in the CEMS. Results show that most of the monitors exhibited significant bias and variance over the months involved. Monitoring data precision varied significantly from month to month and does not appear to be related to monitor type or manufacturer.

Introduction

On June 11, 1979, the EPA promulgated regulations requiring that fossil-fired utilities, built after 1978, use continuous emission monitoring to show continual compliance with new source performance standards.[1] The quality of the monitoring data is of utmost importance in order for source owners/operators and the enforcement agencies to reliably determine compliance. The principal parameters in assessing and describing data quality are accuracy and precision. On March 14, 1984, EPA proposed to add "Appendix F, Quality Assurance Procedures: Procedure 1 - Quality Assurance Requirements for Gas Continuous Emission Monitoring System (CEMS) for Compliance" to 40 CFR 60.[2] The proposed regulation would require the source owner/operator to periodically assess the precision and accuracy of data from each gas CEMS used to show compliance of a continuous basis. The CEMS data precision is estimated using available daily calibration drift data.

This paper discusses the long-term precision for pollutant (SO_2, NO_x) and diluent (O_2, CO_2) monitors included in five CEMS's. The CEMS's are representatives of the types most commonly utilized by the electric utility industry. Six or seven months of data were acquired and analyzed according to procedures specified in the proposed Appendix F, Procedure 1. It is emphasized that precision, as used in this paper, is a measure of the day-to-day variability of a specific monitor in measuring a reference standard. An assessment is made of the precision of the individual monitor and not of the composite monitoring system.

Four of the five CEMS's evaluated are on sources which do not use the CEMS to demonstrate compliance with emission limits. Also, the sources that participated in this study are not subject to any CEMS QA requirements. Thus, the results obtained are not necessarily representative of the improved level of CEMS performance that is likely to be achieved at facilities where mandatory QA/QC requirements (such as those of proposed Appendix F, Procedure 1) are fully implemented.

Precision Assessment Procedures

As specified in the proposed Appendix F, a one-point precision check must be made each day on each pollutant and diluent monitor in a CEMS as follows:

1. Challenge each monitor with a calibration standard (cylinder gas, gas cell, or optical filter) of known concentration value at the span level (i.e., 50-100 percent of span value).

2. Operate each monitor in its normal sampling mode during the precision check.

3. Perform the check immediately before any adjustments are made to the monitor for zero and span drift.

The difference between the actual concentration of the calibration standard and the concentration indicated by the monitor is used to assess the calibration drift and the precision of the monitoring data. The signed percentage difference is computed each day in order to identify a systematic bias or trend in the differences. The percentage difference is used instead of the actual difference because the measure of precision is generally proportional to the concentration level. Thus, it is not necessary that the calibration standard be the same each day. When the calibration drift exceeds four times the applicable performance specification in Appendix B, 40 CFR 60,[3] the monitor is "out-of-control," and the precision check result for that day must be excluded from the calculations.

Calculations for Monitoring Data Precision

Using the upscale calibration drift data, the daily percentage difference (d_i) for each precision check was calculated using Equation 1.

$$d_i = \frac{Y_i - X_i}{X_i} \times 100 \qquad \text{Equation 1}$$

where:

(Y_i) = Monitor indicated concentration from the i-th precision check

(X_i) = Known concentration of the precision check reference used for the i-th precision check.

The monthly average percent difference ($\overline{d}_j$) and standard deviation of the percent differences (S_j) were calculated using Equation 2 and Equation 3, respectively.

$$\overline{d}_j = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad \text{Equation 2}$$

$$S_j = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^{n} d_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} d_i \right)^2 \right]} \qquad \text{Equation 3}$$

where n is the number of valid precision checks on the monitor made during the calendar month.

The upper and lower 95 percent probability limits (UPL and LPL) for precision were calculated by using Equations 4 and 5.

$$UPL = \bar{d}_j + 1.96\, S_j \qquad \text{Equation 4}$$

$$LPL = \bar{d}_j - 1.96\, S_j \qquad \text{Equation 5}$$

Summary and Discussion of Results

A total of 923 and 626 days of calibration drift data were analyzed for six pollutant and four diluent monitors, respectively. Table 1 shows the distribution of the daily precision values (d_i) obtained for each of the monitors. An examination of the data shows that d_i values were less than ± 15% for 915 of the 923 precision checks made on the pollutant monitors (i.e., 99 percent of the reported data). For the diluent monitors, d_i values were less than ± 15% for 613 of 626 precision checks (i.e., 98 percent of the reported data). The d_i values were less than ± 5% for 90 percent of the data reported on diluent monitors, compared to 79 percent of the data reported on pollutant monitors.

Tables 2-6 present the monthly precision data for each of the five CEMS's included in the study. The precision data can be used to determine if a consistent bias exists or if there are any trends or particular patterns in the precision check. A systematic bias exists if

$$t = \sqrt{n}\,\frac{\bar{d}_j}{S_j} \qquad \text{Equation 6}$$

is greater than about 2 in absolute value, where t is the standard t statistic.[4] As shown in the tables, several of the monitors exhibited significant bias during the months involved.

Probability limits provide a means of determining whether a daily precision check value (d_i)indicates the monitor is "out of control"; the monitor-measured concentration is not within the expected deviation from the known concentration of the standard. Assuming an underlying normal distribution of these data, the probability limits would be expected to include about 95 percent of the individual daily precision check values. For one month of data, it is expected that only one of two values would fall outside the probability limits. A d_i outside the probability limits may be a signal that the monitor is not providing data of consistent quality on the i-th day. As shown in the tables, the numbers of daily precision values outside the 95 percent probability limits were generally 2 or less for all of the monitors.

The values of $\bar{d}_j$ and S_j should also be examined over several months to determine the presence of bias and/or trends. A simple plot of $\bar{d}_j$ and S_j versus month should reveal any data anomalies. Even if $\bar{d}_j$ is not significantly different from zero, the daily values of d_i should always be visually checked for a trend or pattern.

The Duncan's multiple range statistical test may be used to compare the monthly mean differences ($\bar{d}_j$). Based on the Duncan's test[5], at the 5 percent level of significance, the monthly means varied significantly for all of the monitors during the six or seven month period. An analysis of the monthly standard deviations (S_j) may also be used to compare the variability of the monthly precision data with time. Based on the Bartlett's statistical test[5], at the 5 percent level of significance, none of the monitors showed monthly variances (S_j^2) that are entirely homogeneous over the time period evaluated. Two of the pollutant monitors (LSI SO_2 and EDC SO_2) showed significantly greater variability than the other monitors.

In summary, the precision of the continuous emission monitors varied significantly from month to month. The variability of the monthly precisions does not appear to be related to instrument type or manufacturer. Biases and variances may vary from month to month due to many factors surrounding the measurement process (e.g., temperature and line voltage).

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TABLE 1. SUMMARY OF DAILY PRECISION CHECKS

Monitors	Number of Precision Checks	Distribution of $\lvert d_i \rvert$ values			
		0-5%	5-10%	10-15%	>15%
DuPont Model 460 - SO_2	146	110	28	6	2
Western Reseach Model 721 - SO_2	159	126	32	1	0
Contraves Model M-100 - SO_2	153	134	19	0	0
LSI Model SM-810 - SO_2	153	145	6	2	0
EDC Model D-1400 - SO_2	153	67	48	32	6
Thermo Electron Model IOAR - NO_x	159 / 923	143 / 725	13 / 146	3 / 44	0 / 8
Thermox - O_2	148	105	23	7	13*
Fuji Electric Model 3200 - CO_2	164	148	16	0	0
Contraves Model M-100 - CO_2	160	150	8	2	0
LSI Model CM-50 - O_2	154 / 626	154 / 557	0 / 47	0 / 9	0 / 13

* All 13 values occurred during one month in which 15 precision checks were made.

TABLE 2. MONTHLY PRECISION DATA: CEMS "A"

	4/83	5/83	6/83	7/83	8/83	9/83	10/83
SO_2 Analyzer[1]							
Number of Precision Checks[3]	26	16	20	21	17	29	17
Mean of Daily Precision, %	-1.1	-2.2	-0.7	-0.7	2.2	-1.6	-0.9
Standard Deviation, %	3.7	4.1	4.7	5.2	6.8	6.5	2.5
Upper Probability Limit, %	6.1	5.9	8.4	9.5	15.6	11.1	4.1
Lower Probability Limit, %	-8.4	-10.2	-9.8	-10.9	-11.3	-14.2	-5.8
t-statistic	1.52	2.15	0.67	0.62	1.33	1.32	1.48
d_i Values Outside 95% Probability Limits	1	0	0	1	2	2	2
O_2 Analyzer[2]							
Number of Precision Checks[3]	26	15	21	24	18	29	15
Mean of Daily Precision, %	0.2	3.7	-3.8	2.1	4.7	3.0	17.8
Standard Deviation, %	3.5	4.8	3.7	3.1	2.5	2.4	6.4
Upper Probability Limit, %	6.7	13.1	3.5	8.2	9.6	7.6	30.2
Lower Probability Limit, %	-6.6	-5.7	-11.1	-4.0	-0.2	-1.7	5.3
t-statistic	0.29	2.99	4.71	3.32	7.98	6.73	10.77
d_i Values Outside 95% Probability Limit	2	0	1	2	1	1	2

[1] DuPont 460 SO_2 analyzer (Span: 0-500 ppm; Calibration value: 200-375 ppm).

[2] Thermox O_2 analyzer (Span: 0-25% O_2; Calibration value: 5-12% O_2).

[3] Data was not used for days when calibration drift exceeded four times drift specifications defined in Appendix B, 40 CFR 60.

TABLE 3. MONTHLY PRECISION DATA: CEMS "B"

	9/83	10/83	1/84	2/84	3/84	4/84
SO_2 Analyzer[1]						
Number of Precision Checks[3]	25	27	27	26	29	25
Mean of Daily Precision, %	-0.8	-0.3	4.9	1.0	-3.3	-0.9
Standard Deviation, %	2.8	3.9	1.6	2.5	2.7	3.0
Upper Probability Limit, %	4.7	7.4	8.1	5.8	1.9	5.1
Lower Probability Limit, %	-6.3	-7.9	1.7	-3.9	-8.6	-6.8
t-statistic	1.43	0.40	15.91	2.04	6.58	1.50
d_i Values Outside 95% Probability Limits	1	3	2	2	1	1
CO_2 Analyzer[2]						
Number of Precision Checks[3]	25	30	27	26	29	27
Mean of Daily Precision, %	0.1	0.4	0.9	-0.4	2.7	-2.3
Standard Deviation, %	1.3	4.1	1.7	1.3	2.6	2.6
Upper Probability Limit, %	2.5	8.4	4.2	2.0	7.8	2.8
Lower Probability Limit, %	-2.4	-7.8	-2.5	-2.9	-2.4	-7.3
t-statistic	0.39	0.53	2.75	1.57	5.59	5.00
d_i Values Outside 95% Probability Limit	0	2	1	3	0	2

[1] Western Research Model 721 SO_2 monitor (Span: 0-500 ppm; Calibration value: 450 ppm).

[2] Fuji Electric Model 3200 CO_2 monitor (Span: 0-20% CO_2; Calibration value: 18% CO_2).

3 Data was not used for days when calibration drift exceeded four times drift specifications defined in Appendix B, 40 CFR 60.

TABLE 4. MONTHLY PRECISION DATA: CEMS "C"

	10/83	11/83	12/83	1/84	2/84	3/84
SO_2 Analyzer[1]						
Number of Precision Checks[3]	20	28	30	30	22	23
Mean of Daily Precision, %	-0.9	0.2	0.1	-0.8	-1.9	-2.0
Standard Deviation, %	0.5	0.7	1.9	1.0	2.8	4.7
Upper Probability Limit, %	0.1	1.6	3.8	1.1	3.6	7.3
Lower Probability Limit, %	-1.9	-1.2	-3.6	-2.7	-7.4	-11.2
t-statistic	8.05	1.51	0.29	4.38	3.18	2.04
d_i Values Outside 95% Probability Limits	0	1	2	3	1	2
O_2 Analyzer[2]						
Number of Precision Checks[3]	18	28	29	30	22	27
Mean of Daily Precision, %	0.0	1.2	2.2	2.7	3.2	0.1
Standard Deviation, %	0.8	1.0	0.8	0.6	1.2	0.6
Upper Probability Limit, %	1.7	3.2	3.8	3.9	5.5	1.2
Lower Probability Limit, %	-1.7	-0.8	0.6	1.4	0.8	-0.9
t-statistic	0.00	6.35	14.81	24.65	12.51	0.87
d_i Values Outside 95% Probability Limit	0	1	0	0	2	2

1 LSI Model SM810 SO_2 monitor (Range: 0-750 ppm; Calibration value: 440 ppm).

2 LSI Model CM-50 O_2 monitor (Range: 0-25% O_2; Calibration value: 21% O_2).

3 Data was not used for days when calibration drift exceeded four times drift specifications defined in Appendix B, 40 CFR 60.

TABLE 5. MONTHLY PRECISION DATA: CEMS "D"

	6/83	7/83	8/83	9/83	10/83	11/83
SO_2 Analyzer[1]						
Number of Precision Checks[3]	27	30	26	24	28	18
Mean of Daily Precision, %	-2.9	-0.8	-0.8	-0.9	-1.6	-2.9
Standard Deviation, %	1.8	3.3	2.5	2.9	2.7	3.5
Upper Probability Limit, %	0.7	5.6	4.1	4.7	3.7	4.0
Lower Probability Limit, %	-6.5	-7.2	-5.7	-6.6	-6.9	-9.8
t-statistic	8.37	1.33	1.63	1.52	3.14	3.52
d_i Values Outside 95% Probability Limits	1	2	1	0	0	0
CO_2 Analyzer[2]						
Number of Precision Checks[3]	27	29	26	24	28	26
Mean of Daily Precision, %	3.3	0.9	2.5	2.7	1.0	0.4
Standard Deviation, %	0.9	5.9	1.8	1.9	2.7	1.8
Upper Probability Limit, %	5.1	12.4	5.9	6.4	6.3	3.8
Lower Probability Limit, %	1.5	-10.7	-1.0	-1.1	-4.7	-3.1
t-statistic	19.05	0.82	7.08	6.96	1.96	1.13
d_i Values Outside 95% Probability Limit	0	2	1	1	2	0

[1] Contraves Model M-100 (Range: 0-750 ppm; Calibration value: 375 ppm).

[2] Contraves Model M-100 (Range: 0-20% CO_2; Calibration value: 10.5% CO_2).

[3] Data was not used for days when calibration drift exceeded four times drift specifications defined in Appendix B, 40 CFR 60.

TABLE 6. MONTHLY PRECISION DATA: CEMS "E"

	7/83	8/83	9/83	10/83	1/84	2/84	3/84
SO_2 Analyzer[1]							
Number of Precision Checks[3]	18	16	26	16	31	25	21
Mean of Daily Precision, %	-4.2	5.4	0.6	1.8	5.5	11.3	4.3
Standard Deviation, %	3.2	8.0	8.6	4.3	2.6	2.0	6.2
Upper Probability Limit, %	2.0	21.0	17.3	10.2	10.7	15.3	16.4
Lower Probability Limit, %	-10.4	-10.2	-16.2	-6.7	0.3	7.4	-7.7
t-statistic	5.57	2.75	0.36	1.67	11.78	28.25	3.18
d_i Values Outside 95% Probability Limits	0	0	1	0	3	0	1
CO_2 Analyzer[2]							
Number of Precision Checks[3]							
Mean of Daily Precision, %							
Standard Deviation, %							
Upper Probability Limit, %							
Lower Probability Limit, %							
t-statistic							
d_i Values Outside 95% Probability Limit							

[1] EDC Model D-1400 (Range: 0-1000 ppm; Calibration value: 270-380 ppm).

[2] CO_2 monitor was out of service during this period.

[3] Data was not used for days when calibration drift exceeded four times drift specifications defined in Appendix B, 40 CFR 60.